

# Atomic topology and radial distribution functions of $\alpha$ -SiN $_x$ alloys. *Ab initio* simulations

Fernando Alvarez and Ariel A. Valladares\*

*Instituto de Investigaciones en Materiales, UNAM, Apartado Postal 70-360, México D.F., 04510, MEXICO*

(06 June 2001)

We report a new approach to simulate amorphous networks of covalently bonded materials that leads to excellent radial distribution functions and realistic atomic arrangements. We apply it to generate the first *ab initio* structures of nitrogen-doped silicon,  $\alpha$ -SiN $_x$ , for thirteen values of  $x$  from 0 to the nearly stoichiometric composition of  $x=1.29$ , using the Harris functional and thermally amorphized, periodically continued, diamond-like cells with 64 atoms. Partial radial features are reported for the first time and the total radial distribution functions agree very well with the few existing experiments. Our results should stimulate further experimental and theoretical studies in amorphous covalent materials.

PACS numbers:71.23.Cq, 71.15.Pd, 71.55.Jv,

## I. INTRODUCTION

The properties of amorphous silicon-nitrogen alloys have attracted a great deal of attention in the last decade;  $\alpha$ -SiN $_x$  has electrical, optical and mechanical features useful in a variety of industrial applications and the strong covalency of their bonding makes them the prototype of covalent materials. Their optical gaps depend strongly on the nitrogen content  $x$  for  $0 \leq x \leq 1.33$  so they can be tuned to fit specific needs in solar cells; their total and partial radial distribution functions (RDFs) are practically unknown, except for the stoichiometric content. Some semiempirical studies have been done on their electronic structure, optical gaps and RDFs and a first-principles approach has been used on an *ad hoc*-generated amorphous structure. Therefore, any *ab initio* approach that adequately generates, describes and predicts features of  $\alpha$ -SiN $_x$  may have a wider applicability to deal with other covalently-bonded amorphous solids; in particular, systems like  $\alpha$ -GeN $_x$  should be amenable to our approach [1].

Recently [2] we carried out *ab initio* Harris-functional-based studies of the atomic and electronic structure of pure and hydrogenated amorphous silicon, using 64 silicon atom cells plus hydrogens that diffuse within the cells. We now apply these methods to amorphous silicon-nitrogen alloys to test the adequacy and the predictive powers of our approach for covalent materials. To the best of our knowledge, these are the first *ab initio* thermally generated amorphous networks where studies of the atomic topology of  $\alpha$ -SiN $_x$  are carried out; the content  $x$  is in the range  $0 \leq x \leq 1.29$  where  $x = y/(64 - y)$  and  $y$  is the number of nitrogen atoms.

The experimental and theoretical activity prior to 1990 is well documented in a paper by Robertson where pertinent references can be found [3]. In this work Robertson reports his semiempirical tight-binding calculations for the optical gaps and also reports several experimental gaps for hydrogenated and non-hydrogenated  $\alpha$ -SiN $_x$  alloys. Bethe lattice calculations have been done by

Martín-Moreno *et al.* [4] and by San-Fabián *et al.* [5] also using semiempirical parameters, whereas Ordejón and Ynduráin [6] in a very nice work do non-parameterized calculations of  $\alpha$ -SiN $_x$  where the equilibrium positions of Si and N atoms in clusters are ported to the alloy network constructed *ad hoc*. They obtain a wealth of information including optical gaps, however tetrahedral coordination of the silicon atoms and threefold planar coordination of the nitrogen atoms is *assumed* with interatomic distances of 2.33 Å for Si-Si and 1.74-1.76 Å for Si-N. A general characteristic of these calculations/simulations is that gap states, when considered, are introduced either by hand, progressively replacing Si by N, or by the algorithms that generate the random networks, *unlike* the procedure reported here. Recent semiempirical classical simulations by de Brito *et al.* [7] produced total RDFs and average nearest-neighbor results that are the subject of comparison with ours.

On the experimental side, as early as 1976 Voskoboynikov *et al.* [8] studied some RDFs and optical gaps of silicon-rich silicon-nitrogen films as a function of the gas ratio. It was then observed that the gaps increase as a function of the nitrogen content; the films seemed to contain hydrogen and large clusters of silicon. However, reliable experimental RDFs are scarce [9] and, apparently, only total ones for the stoichiometric amorphous composition exist [10], where a decomposition of the second peak of the total RDF into its partial contributions is also carried out.

It is clear that the atomic topology also determines the electronic properties of the amorphous samples, and therefore any understanding of the RDFs and the atomic distribution in the random networks is relevant in the characterization of the electronic and optical properties of these materials. In what follows we report the generation of random networks for amorphous silicon nitrogen alloys that leads to RDFs in good agreement with what is known experimentally and predict atomic structures for a variety of nitrogen contents. Electronic gap states are found in these structures that shall be dealt with in

a future publication.

## II. METHOD

Our 26 amorphous samples of  $\alpha$ -SiN $_x$  were generated with *FastStructure* [11], a DFT code based on the Harris functional produced by *Molecular Simulations, Inc.*. The optimization techniques use a fast force generator to allow simulated annealing/molecular dynamics studies with quantum force calculations [12]. The LDA parameterization invoked is that due to Vosko, Wilk and Nusair [13]. An all electron calculation is carried out, and a minimal basis set of atomic orbitals was chosen with a cutoff radius of 5 Å for the amorphization and 3 Å for the optimization. The physical masses of nitrogen and silicon are used throughout and this allows us to see realistic randomizing processes of the atoms during the amorphization of the supercell. Finally, the forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional [14].

In order to test the adequacy of calculations carried out with *FastStructure* we used it to obtain the size of the crystalline cell of  $\beta$ -Si $_3$ N $_4$  that minimizes the energy at the  $\Gamma$ -point. Fig. 1 shows the results of such calculation. The experimental crystalline volumen is given by 145.920 Å $^3$  [15] whereas the calculated volumen is 146.797 Å $^3$ ; a deviation of 0.6%. For this reason we feel cautiously optimistic about the use of *FastStructure* to generate random networks of silicon-nitrogen alloys.

Since it has become increasingly clear that quenching from a melt generates undesirable structures [7] we took a different path [2]. We amorphized the crystalline diamond structures with a total of 64 atoms ((64 -  $y$ ) silicons and  $y$  substitutional nitrogens) in the cell by slowly heating it, linearly, from room temperature to just below the corresponding melting point for each  $x$ , and then slowly cooling it to 0 K. To determine the melting temperatures for each  $x$  we linearly interpolated between the pure silicon value and the stoichiometric compound,  $x = 4/3 = 1.33$ , and then remained below these temperatures (Table I). Since the time step was the same for all runs, 6 fs, and the melting temperatures increased with  $x$ , the heating/cooling rate varied from  $2.30 \times 10^{15}$  K/s for pure silicon, to  $3.11 \times 10^{15}$  K/s for  $x = 1.29$ . The atoms were allowed to move freely within each cell whose volume was determined by the corresponding density and content, Table I. The densities were taken from the experimental results of Guraya *et al.* [9]. Once this first stage was completed, we subjected each cell to annealing cycles with intermediate quenching processes. Finally the samples were energy-optimized to make sure the final structures would be those of a local energy minimum.

**TABLE I**  
Contents, Melting Temperatures and Densities  
for  $\alpha$ -SiN $_x$

Sample	$x$	Melting Temp. (K)	Density (g/cc)
Si $_{64}$ N $_0$	0.000	1680	2.329
Si $_{59}$ N $_5$	0.085	1747	2.435
Si $_{54}$ N $_{10}$	0.185	1814	2.512
Si $_{49}$ N $_{15}$	0.306	1881	2.600
Si $_{44}$ N $_{20}$	0.455	1948	2.694
Si $_{39}$ N $_{25}$	0.641	2015	2.803
Si $_{34}$ N $_{30}$	0.882	2082	2.931
Si $_{33}$ N $_{31}$	0.939	2095	2.957
Si $_{32}$ N $_{32}$	1.000	2108	2.988
Si $_{31}$ N $_{33}$	1.065	2122	3.017
Si $_{30}$ N $_{34}$	1.133	2136	3.048
Si $_{29}$ N $_{35}$	1.207	2149	3.081
Si $_{28}$ N $_{36}$	1.286	2162	3.115

It should be kept in mind that our objective is always to generate realistic amorphous structures of  $\alpha$ -SiN $_x$  and not, in any way, to mimic the experimental processes used to produce these alloys.

## III. RESULTS AND DISCUSSION

We performed two runs for each  $x$  value and from  $x = 0.882$  on ( $\alpha$ -Si $_{34}$ N $_{30}$ ) the number of nitrogens was increased one at a time to be able to map the interesting processes that occur for these contents (percolation of the Si-Si bonds, widening of the optical gaps, etc). Once the atomic structures were obtained, we calculated the corresponding total and partial RDFs for each of the 26 runs and averaged them by corresponding pairs. Of those 13 averaged plots we are reporting here total and partial RDFs for pure silicon, for the almost stoichiometric sample,  $\alpha$ -Si $_{28}$ N $_{36}$ ,  $x = 1.29$ , and two intermediate ones:  $\alpha$ -Si $_{44}$ N $_{20}$ ,  $x = 0.46$  and  $\alpha$ -Si $_{32}$ N $_{32}$ ,  $x = 1.00$ . Fig 2a for the pure amorphous silicon sample shows our results and the upper and lower bounds of the available experimental data [2]; the agreement is good since our RDF falls within these bounds and the four experimental peaks are correctly reproduced by our simulations. Figs. 2b to 2d show the variation of the partial RDFs for Si-Si, Si-N and N-N as a function of content and their contribution to the total RDF. In Fig. 2d the composition of the second peak of the total RDF for the nearly  $\alpha$ -Si $_3$ N $_4$  can be observed and it agrees completely with experiment [16], since it is formed by the average second-neighbor  $\langle 2n \rangle$  contributions of mainly the N-N and Si-Si partials and to a lesser extent by the Si-N partial. The third peak is essentially due to the Si-N partial with a small contribution from the N-N partial but, as far as we know, there are no experimental results for comparison.

Figs. 2 show that as the nitrogen content increases the first peak of the total RDF (1.85 Å), which is due to the Si-N average nearest-neighbor ( $\langle nn \rangle$ ) contributions, increases systematically and the  $\langle nn \rangle$  Si-Si peak (2.45 Å) decreases systematically. The third peak moves toward low  $r$  as  $x$  increases since the N-N contribution becomes more predominant at high content (3.25 Å to 2.95 Å). In our structures there are no  $\langle nn \rangle$  nitrogens since the content is below stoichiometry and nitrogens have a marked tendency to bind to silicons. For the nearly stoichiometric sample,  $x = 1.29$ , the Si-Si  $\langle nn \rangle$  contribution to the total RDF has practically disappeared and this implies that there is a nitrogen atom between every pair of silicons. This is borne out by the results presented in Figs. 3 where a study of the the average coordination numbers  $\langle cn \rangle$  in the 13 random networks is depicted. The following cutoff radii were used: Si-Si, 2.55 Å; N-N, 3.35 Å; and Si-N, 2.15 Å, which are the positions of the minima after the first peaks of the corresponding partials. Fig. 3a shows the results of our simulations where it can be seen that the N-N plot flattens for  $x \approx 1.1$ , the percolation threshold of Si-Si bonds [17]; the Si-Si  $\langle nn \rangle$  go from 4 to practically 0. The Si-N graph refers to the  $\langle nn \rangle$  nitrogens around the silicon atoms and varies from 0 to 4, whereas the N-Si refers to the  $\langle nn \rangle$  silicons around nitrogens and indicates that nitrogens immediately surround themselves with practically 3 Si, saturating its valence. The crossing of the Si-Si and Si-N plots at  $x \approx 0.7$ , is in agreement with experiment (Davis *et al.* [9]). There is a crossing of the Si-Si, N-Si and N-N plots at  $x \approx 0.3$  and a crossing of N-Si and Si-N at  $x \approx 1.0$  which have been observed experimentally for *hydrogenated* alloys by Guraya *et al.* [9], Fig. 3b. However, due to the presence of hydrogen a curvature appears in the  $\langle cn \rangle$  for Si-Si, Si-N and N-Si so, in order to compare our results to this experiment, we did the following. We carried out the sum of N-H plus N-Si from the experiment, the average total number of atoms that surround a N, N-\*, and plotted it along with our N-Si; we also did the sum of the experimental Si-N, Si-Si and Si-H, the average total number of atoms that surround a Si, Si-\*, and plotted that along with our sum of Si-N plus Si-Si. This is presented in Fig. 3c. It is clear that our predictions closely agree with the integrated experimental results and validate our approach. The discrepancies are most likely due to existing dangling and floating bonds.

Fig. 4 is the comparison of our *ab initio* results with the classical Monte Carlo simulations of de Brito *et al.* [7] where they used empirical potentials developed *a la* Tersoff for the interactions between Si and N. It is clear that although the positions of some peaks are reproduced in both simulations, the general behavior of the total RDFs only agree qualitatively. Comparison of each of these simulations with experiment is presented in Fig. 5 where agreements and discrepancies can be appreciated.

## IV. CONCLUSIONS

We have devised an *ab initio* approach for  $\alpha$ -SiN $_x$  ( $0 \leq x \leq 1.29$ ) that generates radial distribution functions in agreement with existing experimental results and realistic atomic structures where the simulated average coordination numbers and the experimental ones coincide. Total RDFs agree very well with experiment, where available, and partial RDFs show that the Si-Si  $\langle nn \rangle$  peak disappears as nitrogen increases indicating a tendency to form 6-atom arrangements as the content  $x$  approaches the stoichiometric value. Experiment shows that for  $\alpha$ -Si $_3$ N $_4$  Si and N form closed rings, Si-N-Si-N-Si-N, typical of the crystalline  $Si_3N_4$  structures. The growth of the Si-N peak as nitrogen increases bears out this behavior. No nitrogen-nitrogen bonds, including molecular nitrogen, are observed in the final structures even though for  $x > 1$  the starting diamond structure *does* contain nitrogens next to one another. For  $x \approx 1.1$  the effects of the percolation threshold of the Si-Si bonds is observed in the N-N  $\langle 2n \rangle$ . For  $x \approx 0.7$  the Si-Si and Si-N neighbors are practically the same, as found experimentally. Also, Si-Si, N-Si and N-N are practically the same for  $x \approx 0.3$  as are Si-N and N-Si for  $x \approx 1.0$ . The integrated experimental results and our simulation agree. The first prominent peak in the total RDF of the nearly stoichiometric sample is due to Si-N and an analysis of the second peak indicates that N-N, Si-Si and Si-N contribute to it, in agreement with experiment. The third peak is mainly due to the Si-N, with a small contribution from the N-N; no experimental results exist for comparison. Our approach, being *ab initio*, is of wider applicability than classical or semiempirical ones and should be relevant for the understanding of the physics of amorphous covalent materials.

## ACKNOWLEDGMENTS

AAV thanks DGAPA-UNAM for financing the project IN101798 and a sabbatical stay at MSI-San Diego, USA, where this work was begun. FA thanks CONACyT for supporting his PhD studies. This work was done on an Origin 2000 computer provided by DGSCA, UNAM.

---

\* Corresponding author; e-mail:valladar@servidor.unam.mx

- [1] Venezuela P.P.M. and Fazzio A. Phys. Rev. Lett., **77** (1996) 546.
- [2] Valladares A.A., Alvarez F., Liu Z., Stitch J. and Harris J. *to be published*.
- [3] Robertson J., Philos. Mag. B, **63** (1991) 47.

- [4] Martín-Moreno L., Martínez E., Vergés J.A. and Ynduráin F. Phys. Rev. B, **35** (1987) 9 683.
- [5] San-Fabián E., Louis E., Martín-Moreno L. and Vergés J.A. Phys. Rev. B, **39** (1989) 1 844.
- [6] Ordejón P. and Ynduráin F. J. Non-Cryst. Solids, **137&138** (1991) 891.
- [7] de Brito Mota F., Justo J.F. and Fazzio A. Phys. Rev. B, **58** (1998) 8 323. de Brito Mota F., Justo J.F. and Fazzio A. Int. J. Quantum Chem., **70** (1998) 973. de Brito Mota F., Justo J.F. and Fazzio A. J. Appl. Phys., **86** (1999) 1 843. Justo J.F., de Brito Mota F. and Fazzio A. *Multiscale Modelling of Materials. Symposium, Mater. Res. Soc.* (1999) p. 555.
- [8] Voskoboinikov V.V., Gritsenko V.A., Dikovskaya N.D., Saitsev B.N., Mogilnicov K.P., Osadchii V.M., Sinita S.P. and Edelman F.L. Thin Solid Films, **32** (1976) 339.
- [9] Hasegawa S., Matuura M. and Kurata Y. Appl. Phys. Lett., **49** (1986) 1 272; Davis E.A., Piggins N. and Bayliss S.C. J. Phys. C, **20** (1987) 4 415; Guraya M.M., Ascolani H., Zampieri G., Cisneros J.I., Dias da Silva J.H. and Cantão M.P. Phys. Rev. B, **42** (1990) 5 677; Santana G., Morales-Acevedo A. Solar Energy Materials & Solar Cells, **60** (2000) 135.
- [10] Aiyama T., Fukunaga T., Niihara K., Hirai T., Suzuki K. J. Non-Cryst. Solids, **33** (1979) 131.
- [11] *FastStructure\_SimAnn, User Guide*, Release 4.0.0 (San Diego, Molecular Simulations, Inc., September 1996).
- [12] Li X-P, Andzelm J., Harris J. and Chaka A.M. *American Chemical Society, Anaheim Symposium* [Ed. Ziegler], Chapter 26, (1996).
- [13] Vosko S.H., Wilk L. and Nusair M. Can. J. Phys., **58** (1980) 1 200.
- [14] Lin Z. and Harris J. J. Phys. Condens. Matter, **4** (1992) 1 055.
- [15] Wild S., Grieseson P. and Jack K.H. *The crystal structure of alpha and beta silicon and germanium nitrides*. Special Ceramics, (1972) 385.
- [16] Misawa M., Fukunaga T., Niihara K., Hirai T. and Susuki K. J. Non-Cryst. Solids, **34** (1979) 313.
- [17] Martínez E. and Ynduráin F. Phys. Rev. B, **24** (1981) 5 718.

Figure1. Energy vs volume for crystalline beta-Si<sub>3</sub>N<sub>4</sub> obtained with FastStructure and experimental values taken from Wild et al. (see text). The experimental and calculated volumes agree to within 0.6%.

Figure2. Total and partial RDFs for (a) pure silicon; the light curves are the upper and lower experimental bounds (Ref. [2]); (b) a-Si<sub>44</sub>N<sub>20</sub>, x=0.46; (c) a-Si<sub>32</sub>N<sub>32</sub>, x=1.00; (d) the nearly stoichiometric sample a-Si<sub>28</sub>N<sub>36</sub>, x=1.29.

Figure3. Average coordination numbers  $\langle cn_i \rangle$  as a function of x. (a) Our results. (b) Experimental results for hydrogenated alloys from Guraya et al.. (c) Comparison of the integrated results (see text). Lines are drawn as guides to the eye.

Figure4. Comparison of our results and those obtained by de Brito et al. (Ref. [7]) for the total RDF. The agreement is at best qualitative although the position of some of the peaks coincide.

Figure5. (a) Comparison of our simulations and experiment (Ref. [10]) for the stoichiometric sample. (b) Comparison of de Brito's simulations and experiment for the same sample.









